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Diacidobis(biguanidinium)Ir(III) Complexes

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Preparation and characterization of *cis*- and *trans*-$[Ir(BigH^+)_2X_2]^+$, where $BigH^+ = C_2H_7N_5^+$ and $X = Cl^-$, Br^-, I^-, NCS^- or NO_2^-, are described. Geometric assignments have been made on the basis of electronic and IR spectral data. Heterochelates, $[Ir(BigH^+)_2\ bipy]^{3+}$ and $[Ir(BigH^+)_2$-phen$]^{3+}$, have also been prepared.

WE have reported earlier the tri chelated complexes of Rh(III) and Ir(III) with biguanide[1,2] and the *cis*-diacidobis(biguanidinium)Rh(III) complexes[3]. In this paper we report the preparation and characterization of the complexes of corresponding diacidobis(biguanidinium)Ir(III) series, in both the geometric forms.

Delepine[4] has observed that ethanol in the reaction medium containing the less basic amine ligands and MCl_6^{3-} [where M = Rh(III) or Ir(III)] catalyses the formation of *trans* dichlorotetraamine metal (III) complexes. Hypophosphorus acid is also known[5] to catalyse the formation of *trans* dichlorotetraamine Ir(III) complexes. Biguanide is a stronger base ($pK_1 = 11{\cdot}52$) than ammonia[6] and we have observed[7] that *trans* dichlorobis(biguanidinium)Rh(III) chloride could be isolated if the reaction between $RhCl_3.3H_2O$ (1*M*) and the free biguanide base (2*M*) was carried out in ethanol. The reaction between biguanidinium hydrochloride and $RhCl_3.3H_2O$ in the aqueous medium in the presence of HCl, however, afforded the *cis* isomer[3]. These observations led us to synthesize dichlorobis-(biguanidinium)Ir(III) species in both the geometric forms.

Materials and Methods

$(NH_4)_2IrCl_6$ was prepared as described in the literature[8]. The method of Holter and Fernelius[9] was adopted for the preparation of biguanidinium sulphate dihydrate ($C_2H_7N_5.H_2SO_4.2H_2O$). Biguanidinium hydrochloride was obtained in aqueous solution by the action of $BaCl_2$ on the ligand acid sulphate.

Electrical conductances were measured using WTW conductivity bridge, type LBR. Electronic absorption spectra were recorded on a Hilger & Watts Uvispek spectrophotometer model H700. IR spectra were recorded in KBr on a Perkin-Elmer 237 infrared spectrophotometer. Thermogravimetric study was performed on a Stanton TR-01 thermobalance with a heating rate of 250°/hr.

Preparation of complexes: *trans*-$[Ir(BigH^+)_2Cl(H_2O)]$-Cl_2 — A solution of 0·0025 mole (0·36 g) of $(NH_4)_2$-$C_2O_4.H_2O$ in 50 ml of boiling water was added in 5 ml portions, with continuous stirring, to 0·005 mole (2·21 g) of $(NH_4)_2IrCl_6$. The solution was boiled for 10 min and filtered. To the filtrate were added 30 ml of ethanol followed by 0·01 mole of biguanidinium hydrochloride in 50 ml of water. The mixture was then refluxed on a water-bath for 6 hr during which time an olive-green product gradually separated. It was allowed to cool to room temperature, the product filtered, wa hed with cold water and dried in air; yield 0·55 g (20%).

trans-$[Ir(BigH^+)_2Cl_2]Cl$ — The dull red filtrate remaining after the removal of the chloroaquo complex was evaporated slowly on a steam-bath to 50 ml, and then left overnight at room temperature when the yellow *trans*-$[Ir(BigH^+)_2Cl_2]Cl$ separated. The product was removed by filtration, washed with cold water and dried in air; yield 1·20 g (48%).

The filtrate upon further evaporation at room temperature yielded a mixture of *trans* and *cis* isomers. After rejecting a few fractions the more soluble light buff-coloured *cis*-$[Ir(BigH^+)_2Cl_2]Cl$ was gradually deposited; yield 0·2 g (8%).

cis-$[Ir(BigH^+)_2Cl_2]Cl$ —$(NH_4)_2IrCl_6$ (0·005 mole) was reduced as above and a few drops of conc. HCl were added (pH, 1·00). To this solution, solid NaCl (0·025 mole, fivefold excess) and biguanidinium hydrochloride (0·01 mole) in 50 ml of water were added. The mixture was then refluxed for 6 hr on a water-bath. The resulting solution gave light buff-coloured *cis*-$[Ir(BigH^+)_2Cl_2]Cl$ on evaporation and cooling to room temperature. This was collected, washed and dried in the usual way; yield 1·88 g (76%).

Sulphate derivatives of both *cis* and *trans* dichloro complexes were obtained by metathesis with Ag_2SO_4.

cis and *trans* dibromo-, diiodo-, dinitro- and diisothiocyanato- complexes were obtained by refluxing the *cis* or *trans* dichloro complex with the corresponding sodium salts and cooling the concentrated solution. With NaN_3 only *trans*-$[Ir(BigH^+)_2Cl_2]N_3$ could be isolated on refluxing for 15 min. On prolonged refluxing, both *cis* and *trans* dichloro complexes hydrolyse. All the complexes except the chloroaquo and dichloro azide were recrystallized from hot water.

The heterochelates $[Ir(BigH^+)_2bipy]Cl_3$ and $[Ir-(BigH^+)_2phen]Cl_3$ were obtained by refluxing *cis*-

$[Ir(BigH^+)_2Cl_2]Cl$ and the respective base hydrochloride in aqueous medium in the molar ratio of 1:1 on a water-bath with slow addition of aqueous KOH (*p*H, 7·00). Both the heterochelates were recrystallized from hot water and collected and dried in the usual way.

Results and Discussion

Analytical data of the complexes are given in Table 1. Thermogravimetric study of the olive-green $[Ir(BigH^+)_2Cl(H_2O)]Cl_2$ shows that the coordinated water is slowly lost between 70° and 100° with the formation of a light yellow water-soluble product, $[Ir(BigH^+)_2Cl_2]Cl$. This was identified as the *trans* isomer by comparison with the IR spectrum of *trans*-$[Rh(BigH^+)_2Cl_2]Cl$.

The formation of *trans*-$[Ir(BigH^+)_2Cl(H_2O)]Cl_2$ as well as of *trans*-$[Ir(BigH^+)_2Cl_2]Cl$ could be avoided on carrying out the reaction between $(NH_4)_3IrCl_6$ (1 mole) and biguanidinium hydrochloride (2 moles) in the presence of HCl (*p*H, 1·00) and fivefold excess of NaCl. The resulting dull red solution yielded the light buff *cis*-$[Ir(BigH^+)_2Cl_2]Cl$ (yield 75%) on evaporation and cooling to room temperature. Such stereospecific synthesis using very high chloride ion strength has been reported by Bauer and Basolo[10] in the case of *cis*-$[Ir(en)_2Cl_2]Cl$.

cis and *trans* dibromo, diiodo, diisothiocyanato and dinitro derivatives were prepared from the respective dichloro isomers by anion substitution reactions. Substitution reactions of the *cis* complexes are quite rapid as compared to those of the *trans* complexes. No diazido could be synthesized by this technique. The geometric assignments of these were made on the basis of their electronic and IR spectra and the formation of mixed chelates with 2,2′-bipyridyl and 1,10-phenanthroline in the case of *cis* isomer.

The electronic absorption spectra of the dichloro species in aqueous solution show the characteristic differences between *cis* and *trans* isomers. The *cis* isomer shows bands at 390 and 290 nm with extinction coefficients of 71 and 658 $mole^{-1}$ cm^{-1} respectively while the *trans* isomer shows bands at 411 and 316 nm with extinction coefficients of 51 and 482 $mole^{-1}$ cm^{-1} respectively. The high extinction coefficient band is observed at higher frequency for *cis* complex as compared with the *trans* complex in conformity with the general behaviour of *cis* and *trans* isomers.

The IR spectra of the compounds generally resemble those of their Rh(III) analogues but *cis* isomers in each case show a high degree of splitting for bands around 3200, 1600 and 800 cm^{-1}. The NH_2 asymmetric deformation (1600 cm^{-1}) bands[11] of various diacido complexes support the formulations shown in Table 2. The *trans* isomers contain a single sharp peak as compared to the well-resolved doublet for *cis* compounds.

Further, *cis* and *trans* geometries could be successfully assigned to the dinitro species following the method of Chatt *et al.*[12]. The *cis* isomer shows ν_s NO_2 at a lower frequency than the *trans* isomer (Table 3).

The IR spectra of the diisothiocyanato complexes are somewhat different and indicate the presence of N-bonded and ionic thiocyanate ions[13]. [*cis*: ν(CN) 2110 vs, 2042 vs; ν(CS) 810 m, 776 m; *trans*: ν(CN) 2093 vs, br; ν(CS) 807 m, 768 m].

In the far infrared region, two νIr—X bands were recorded for the *cis*-dichloro (302, 312 cm^{-1}) and dibromo (180, 198 cm^{-1}) as compared to one band in the case of *trans* isomers[14] (dichloro, 310 cm^{-1}; dibromo, 201 cm^{-1}). This is in agreement with the behaviour of corresponding Rh(III) complexes where the *cis* dichloro isomer shows two bands at 301 and 268 cm^{-1} while the *trans* isomer shows one band at 279 cm^{-1}.

The *cis* dichloro complex chloride shows lower conductance value (*cis*: 96·23; *trans*: 97·58 mhos cm^2 $mole^{-1}$ in water at 25°) probably due to greater tendency for ion-pair formation[15,16]. A preliminary

TABLE 1 — ELEMENTAL ANALYSES OF THE COMPLEXES

Compound	Colour	Ir (%)		N (%)	
		Found	Calc.	Found	Calc.
trans-$[IrL_2Cl(H_2O)]Cl_2$*	Olive green	37·21	37·05	26·88	27·00
trans-$[IrL_2Cl_2]Cl$*	Yellow	38·50	38·38	27·32	27·97
cis-$[IrL_2Cl_2]Cl$*	Light buff	38·47	38·38	27·28	27·97
trans-$[IrL_2Cl_2]\frac{1}{2}SO_4$	Yellow	37·67	37·43	27·02	27·28
cis-$[IrL_2Cl_2]\frac{1}{2}SO_4$	Light yellow	37·51	37·43	27·30	27·28
trans-$[IrL_2Cl_2]N_3$	Bright yellow	38·01	37·88	36·00	35·87
trans-$[IrL_2Br_2]Br$	Bright yellow	30·28	30·31	22·23	22·09
cis-$[IrL_2Br_2]Br$	Yellow	30·61	30·31	22·21	22·09
trans-$[IrL_2I_2]I$	Rust brown	24·91	24·80	18·05	18·07
cis-$[IrL_2I_2]I$	Reddish brown	25·01	24·80	18·13	18·07
trans-$[IrL_2(NCS)_2]SCN$*	Deep yellow	—	—	32·31	32·02
cis-$[IrL_2(NCS)_2]SCN$*	Deep yellow	—	—	32·26	32·02
trans-$[IrL_2(NO_2)_2]NO_2$	Pale yellow	36·15	36·06	34·22	34·18
cis-$[IrL_2(NO_2)_2]NO_2$	Pale yellow	36·18	36·06	34·31	34·18
$[IrL_2bipy]Cl_3$*	Yellowish brown	29·65	29·25	25·62	25·58
$[IrL_2phen]Cl_3$*	Yellowish brown	28·15	28·22	24·75	24·68

L = $BigH^+ = C_2H_7N_5$.
*Satisfactory C and H analyses were also obtained.

TABLE 2 — IR BANDS IN NH_2 ASYMMETRIC DEFORMATION REGION (cm^{-1})

Complex	*trans*	*cis*
$[Ir(BigH^+)_2Cl(H_2O)]Cl_2$	1619	—
$[Rh(BigH^+)_2Cl_2]Cl$	1618	1615, 1595
$[Ir(BigH^+)_2Cl_2]Cl$	1620	1614, 1585
$[Ir(BigH^+)_2Br_2]Br$	1609	1611, 1590
$[Ir(BigH^+)_2I_2]I$	1605	1619, 1600
$[Ir(BigH^+)_2(NCS)_2]SCN$	1610	1630, 1608
$[Ir(BigH^+)_2(NO_2)_2]NO_2$	1612	1627, 1608

TABLE 3 — INFRARED SPECTRAL BANDS OF NO_2 GROUP (cm^{-1})

Compound	ν_3 (asym str.)	ν_1 (sym str.)	ν_2 (bending)
trans-$[Rh(BigH^+)_2(NO_2)_2]NO_2$	1382 s	1345 s	819 s
trans-$[Ir(BigH^+)_2(NO_2)_2]NO_2$	1403 s	1320 s	829 s
cis-$[Rh(BigH^+)_2(NO_2)_2]NO_2$	1385 s	1331 ms	835 s
		1350 s	829 s
cis-$[Ir(BigH^+)_2(NO_2)_2]NO_2$	1388 s	1310 s	820 s
		1338 s	828 s

X-ray powder pattern shows that they have different crystal structures, the *trans* isomer appears to be tetragonal while *cis* is triclinic.

cis-$[Ir(BigH^+)_2Cl_2]Cl$, like its Rh(III) analogue[3], undergoes substitution with 2,2′-bipyridyl and 1,10-phenanthroline when the complex and the respective base hydrochloride are heated in 1:1 molar ratio in aqueous solution and the *p*H is gradually raised to 7 by slow addition of aqueous KOH. The heterochelates $[Ir(BigH^+)_2bipy]Cl_3$ and $[Ir(BigH^+)_2phen]Cl_3$ are more soluble than the dichloro complexes showing molar conductance values of 388 and 382 mhos cm^2 $mole^{-1}$ respectively in water at 25°. This supports their formulation as 1:3 electrolytes.

The *cis*-$[Ir(BigH^+)_2Cl_2]Cl$ could not be resolved into its optical isomers by the formation of diastereoisomers with the ammonium salt of (+)-α-bromocamphor-π-sulphonic acid. This may perhaps be due to almost similar solubility of the diastereoisomers, as the racemic mixture itself has very low solubility (0·2 g/100 ml) compared to *cis*-$[Ir(en)_2Cl_2]Cl$ (5·3 g/100 ml) in H_2O at room temperature[10].

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